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(54) **INTERPOLYMERS OF ETHYLENE AND UNSATURATED CARBOXYLIC ACIDS**

INTERPOLYMERE VON AETHYLEN UND UNGESÄTTIGTEN SÄUREN

INTERPOLYMERES D'ETHYLENE ET D'ACIDES CARBOXYLIQUES NON SATURES

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Description

BACKGROUND

[0001] Interpolymers of ethylene and unsaturated carboxylic acids, such as acrylic acid and methacrylic acid, are well known. This present disclosure pertains to a process for producing such interpolymers when made under steady state conditions in stirred reactors at high pressure and elevated temperature and using a free-radical type initiator, in contradistinction to polymers made under non-steady state conditions or in non-stirred tubular reactors or in batch reactions, and in contradistinction to block copolymers or graft copolymers.

[0002] Patents which disclose interpolymerizations of ethylene and unsaturated carboxylic acids in a steady state reaction at high temperature and high pressure in a stirred reactor in the presence of a free-radical initiator are, e.g., Canadian Patent 655,298 (and its U.S. counterpart No. 4,351,931): U.S. 3,239,370; U.S. 3,520,861; U.S. 3,658,741; U.S. 3,884,857; U.S. 3,988,509; U.S. 4, 248,990; and U.S. 4,252,924.

[0003] U.S. 3,239,370 discloses a random copolymerization of ethylene with an unsaturated carboxylic acid (e.g. acrylic acid) in a stirred autoclave operated at 112.5 M Pa (16000 psi), and 210°C using a peroxy initiator, the so-formed copolymer being particularly useful as a coating for non-metallic substrates.

[0004] U.S. 3,520,861 discloses a substantially homogeneous, compositionally uniform, random copolymer of ethylene/unsaturated acid (e.g. acrylic acid, methacrylic acid, crotonic acid) prepared in a continuous manner in a stirred autoclave at high pressure and elevated temperature, using a free-radical initiator (such as a peroxide). The temperature of the polymerization is disclosed as being in the range of about 120° C to about 300° C, preferably about 150° C to about 250° C. The pressure of the polymerization is disclosed as being in the range of at least 98.1 M Pa (1000 atmospheres), preferably between about 98.1-294.3 M Pa (1000-3000 atmospheres), esp. between 107.9-186.4 M Pa (1100-1900 atmospheres).

[0005] Canadian Patent No. 655,298 and its U.S. counterpart (U.S. 4,351,931) discloses homogeneous, compositionally uniform, random copolymers of ethylene and unsaturated carboxylic acids (e.g. acrylic acid) wherein said copolymer comprises at least about 90% by weight of ethylene with a melt index of 0.01 to 30 g/10 minutes. The copolymers are prepared in a well-stirred reactor at a pressure of at least 98.1 M Pa (1000 atmospheres), at 90°-280°C, using a free radical initiator, while maintaining the ratio of monomers (ethylene/acid) in the range of 10,000/1 to 50/1 by weight, the process being performed continuously by feeding monomers in, while removing reaction mixture, and maintaining a constant reaction environment.

[0006] U.S. 3,658,741 discloses homogeneous copolymers of ethylene and unsaturated carboxylic acids and esters, prepared in the presence of a chain transfer agent, a free radical catalyst, a temperature between 100°C-300°C and pressure between 9.81-98.1 M Pa (100 and 1000 atmospheres), using turbulent agitation; the reaction is said to take place in the vapor phase and prepares very low mol. wt. copolymers.

[0007] U.S. 3,884,857 and U.S. 3,988,509 disclose the preparation of copolymers, such as ethylene/acrylic acid copolymers in a continuous, high pressure, free-radical polymerization process, at 100°-250°C and 98.1-245.25 M Pa (1000-2500 atmospheres) of pressure.

[0008] U.S. 4,248,990 discloses copolymers, e.g. ethylene/acrylic acid copolymers which are said to distinguish over the random copolymers of Canadian 655,298 and of U.S. 3,520,861 by virtue of being non-random. This non-randomness is said to be the result of operating the steady state, high pressure, stirred reactor at a pressure of from 0 to about 3.5 M Pa (500 psi) above, and at temperature of from 0°-15°C above, that needed to maintain a single phase reaction mixture at the given concentration of copolymer in the reaction mixture and at the given acid comonomer content of the copolymer.

[0009] U.S. 4,252,924 discloses the preparation of non-random copolymers, e.g. ethylene/acrylic acid copolymers in at least two constant environment, stirred autoclaves in series, each using a single phase reaction mixture, but where each succeeding autoclave is maintained at a temperature of at least 30° C above that of the preceding autoclave.

[0010] In the ordinary course of events, operators of processes are not inclined to employ more energy (temperature and/or pressure) than is deemed necessary to obtain a given product, in the absence of any recognized benefit to be derived from such additional expense. We have now found that there are unexpected benefits to be derived from employing more energy (temperature and pressure) than is generally deemed to be sufficient in the production of interpolymers of ethylene.

SUMMARY OF THE INVENTION

[0011] With reference to random interpolymers of ethylene and olefinically-unsaturated organic comonomers prepared in a well-stirred autoclave, in the presence of a free-radical initiator, under substantially constant conditions of temperature and pressure and substantially steady state, continuous operation, it has now been found, surprisingly and unexpectedly, that substantial and useful improvements are found by maintaining the synthesis conditions of temperature and pressure

elevated high enough above the phase boundary that exists between the two-phase and single-phase conditions, for a given comonomer concentration and polymer concentration in the polymerization mixture, to reach, and/or surpass the respective molecular weight distribution (MWD) boundary, i.e., the synthesis conditions at which the ratio of the weight average mol. wt/number average mol. wt. is at its maximum.

DETAILED DESCRIPTIONS

[0012] Figure 1 is presented as a visual aid for relating the present inventive concept.

[0013] In Figure 1 it is shown that as the synthesis conditions are increased substantially beyond the conditions at which the phase boundary is exceeded and at which single phase operation is achieved, there is found an increase in the ratio of weight average molecular weight (MW_w) to number average molecular weight (MW_n), i.e. a broadening of the MWD occurs, until a molecular weight distribution (MWD) boundary is reached and then surpassed. Referring to Figure 1, the increase in the ratio of MW_w/MW_n is found to be accompanied by beneficial changes in the properties of films and products made from copolymers which are prepared at temperatures above, and pressures well above, the synthesis conditions at which the phase boundary is reached, and also above the non-randomness range disclosed in U.S. 4,248,990; even further beneficial effects are found beyond the MWD boundary where the MWD is found to decrease and the MW_w/MW_n ratio is narrowing.

[0014] Whereas the present inventive concept is perceived as being broadly applicable to interpolymers of ethylene and olefinically-unsaturated organic comonomers, where ethylene comprises the majority amount of the monomer mixture, it is especially applicable to acrylates, methacrylates, vinyl esters, and olefinically unsaturated carboxylic acids as comonomers. It is most especially applicable, and preferably used, in preparing polymers of ethylene interpolymerized with acrylic acid or methacrylic acid. The ensuing descriptions reflect this preference of acrylic acid and methacrylic acid as comonomers.

[0015] This disclosure pertains to a process for preparing improved, homogeneous, random ethylene copolymers, especially to improved copolymers of ethylene and carboxylic acid comonomers. It is an objective of this invention to provide a possibility to produce ethylene copolymers which are especially well suited for adhesive, coating and/or packaging purposes and as extrusion resins. The objectives of the present invention are accomplished by preparing, especially, a copolymer of ethylene and 0.1-35 weight percent of an α,β-ethylenically unsaturated carboxylic acid (e.g., acrylic acid and methacrylic acid) having a melt index in the range of 0.01 to about 5000 g/10 min (ASTM D1238E). By "homogeneous, random", it is meant that substantially all of the copolymer molecules have substantially the same chemical composition although their molecular weight can vary, and that the copolymer has a ratio of weight percent adjacent acid to total weight percent carboxylic acid in the copolymer less than 0.44 (as determined in accordance with U.S. 4,248,990).

[0016] The copolymers prepared according to the present invention combine toughness, flexibility and chemical resistance with outstanding transparency, increased heat seal strength, Improved not tack strengm, excellent extrusion coating properties and reduced microgel levels. One of the surprising attributes of the copolymers prepared according to the present invention is the outstanding transparency obtained at relatively low comonomer concentrations (i.e., <10 percent by wt.). At such low concentrations, the copolymers exhibit transparency ordinarily achievable only at high acid concentrations or via the additional preparation step of acid-salt neutralization, e.g. as described in U.S. 3,264,272, U.S. 4,248,990, and U.S. 4,351,931. Thus, these copolymers are extremely useful as high clarity blown films in such applications as flexible packaging where the additional advantages of exceptional draw-down, handleability, adhesiveness and printability (without corona or other forms of pretreatment) as well as excellent processability are observed.

[0017] The interpolymers prepared according to this invention can also be readily prepared with molecular weight distributions (determined by gel permeation chromatography, which may require esterification pretreatment) suitable for coating applications where improved draw rates, adhesion and heat seal strengths are observed.

[0018] The previous ethylene/carboxylic acid copolymers commonly known in the art normally exhibit poor blown film optical properties that preclude their widespread utilization in some packaging applications. Therefore, the known art of acid-salt neutralization for the preparation of "ionomers" is sometimes employed to confer substantial transparency to the acid copolymer. However, ionomer preparation tends to compromise some of the bulk adhesiveness by "neutralizing" carboxyl or acid groups imparting the adhesion. Routinely, blown film converters, coaters and laminators must pretreat the ionomer product to regain adequate adhesion. Other disadvantages of the known route to transparent, adhesive film grade or coating grade products is the fact that the ionomer is rheologically harder to process on conventional polyethylene extrusion equipment (i.e., ionomers draw high amperages and require additional extruder cooling) and is detrimentally moisture sensitive.

[0019] The lack of transparency exhibited by commercially known copolymers indicates that these products are characterized by comparatively broad molecular weight distributions and/or inadequate homogeneity. Pieski and Sashihara (U.S. Patent 4,248,990) teach copolymer homogeneity as an attribute of single-phase synthesis. Therefore, to prepare the homogeneous (but non-random) copolymers of U.S. 4,248,990, the position of the phase boundary (i.e., the transition

from two-phase to single-phase reaction conditions) must be identified, and the reaction zone must be maintained in steady state at a reactor pressure of from 0 to about 3.5 M Pa (500 psi) above, and at a reactor temperature of from 0° to about 15°C above, that transition point.

[0020] The improved homogeneity of the "single-phase" products described in U.S. 4,248,990 is evidenced by lower levels of micro-gels or "grain" than comparable "two-phase" products. However, these "single-phase" products still possess a fair amount of grain due to their preparation at synthesis conditions in the close proximity of their respective phase boundaries. Such "single-phase" products will also show broader molecular weight distributions (than comparable "two-phase" products) with a subsequent decrease in transparency, and hence, require acid-salt neutralization to achieve the transparency needed for a variety of packaging applications. The broad molecular weight distributions of these "single-phase" products, which are not offset by improved homogeneity, also result in a decrease in the maximum draw rate for film, filament, or coatings as compared to comparable two-phase products.

[0021] At synthesis temperatures and pressures above the range specified by Pieski and Sashihara, the resultant single-phase products are said to be random (versus non-random) as indicated by lower ratios of percent adjacent acid to total weight percent carboxylic acid. Such single-phase products (like those prepared at synthesis conditions in the specified range directly above the phase boundary) are assumed to possess increasingly broader molecular weight distributions as reactor temperature and pressures are progressively increased.

[0022] With reference to Figure 1, which plots the MW_w/MW_n ratio vs. synthesis conditions, there is illustrated a curve which reaches an apex that is labeled as the MWD boundary. Near the lower end of the curve corresponding to the lower end of the synthesis conditions, there is shown a phase boundary between two-phase conditions and single-phase conditions. The two-phase portion of the curve is labeled as 1. The non-random single-phase portion disclosed by Pieski and Sashihara (U.S. 4,248,990) is labeled as 2, and represents the relative position of the curve (not drawn to scale) for copolymers made at 0-3.5 M Pa (0-500 psi) above, and 0-15°C above, the process conditions at which the phase boundary occurs. All the products made at synthesis conditions above the phase boundary are single-phase products. The part of the curve labeled as 3 represents the relative position of the curve between the non-random single-phase portion (2) and the MWD boundary which lies in the random single-phase portion. Beyond the MWD boundary there is a portion of the random single-phase curve labeled as 4 to represent products having a ratio falling approximately in the same range as portions 2 and 3, but which have unexpected improved properties. A curve portion 5 represents products having about the same ratios one would obtain at the two-phase conditions, but which are an appreciable improvement over the two-phase products. Still referring to Figure 1, the product improvements found on both sides of the MWD boundary, but substantially above the process conditions which give the non-random products, are within the purview of the present invention, especially those products in portions 4 and 5 of the ratio curve.

[0023] In accordance with the present invention, homogeneous, random single-phase ethylene copolymers with significantly improved transparency, heat seal strength and hot tack strength, and with molecular weight distributions similar to two-phase products, are readily prepared well above the position of the phase boundary and above the range of non-randomness disclosed in U.S. 4,248,990. Analogous to the phase boundary, we have found that there exists a transition boundary from broad molecular weight distributions to narrow molecular weight distributions. Unlike the phase boundary, the molecular weight distribution (MWD) boundary is not identified by the dramatic changes in initiator demand (efficiency), or by the significant changes in reactor stirrer motor amperage that are well-known to those skilled in the art. However, this position can be conveniently identified at a given comonomer concentration by observing the discontinuity in molecular weight distribution at a constant product melt index and comonomer concentration as synthesis conditions are changed in a manner to pass through the molecular weight distribution (MWD) boundary (Figure 1). Before reaching this molecular weight distribution (MWD) boundary, random single-phase products exhibit broader molecular weight distributions than comparable two-phase products and non-random single-phase products. However, as the MWD boundary is approached, the random single-phase products will exhibit homogeneity that, surprisingly, offsets their broad molecular weight distributions and permits significantly improved transparency, heat seal strengths and drawdown rates. When synthesis conditions are increased further and/or progressively above the MWD boundary, the respective molecular weight distribution correspondingly narrows, i.e., the ratio of MW_w/MW_n decreases. Therefore, it is possible to conveniently prepare "single-phase" products with molecular weight distributions equivalent to "two-phase" products by employing the appropriate synthesis conditions and consequently obtain additional product property improvements. The random single-phase products that are prepared under synthesis conditions at which the MWD boundary is reached, or surpassed are further distinguished from the previously known non-random single-phase products, and the random two-phase products, in that the products prepared according to the processof the present invention, at equivalent comonomer concentrations and polymer concentration in the polymerization mixture, will possess a ratio of weight average mol. wt. to number average mol. wt. as defined by

$$\log\left(\frac{MW_w}{MW_n}\right) = [C_1+(C_2)(\text{wt. fraction comonomer})]$$

where
MW_w is the wt. ave. mol. wt.,
MW_n is the no. ave. mol wt.,
C_1 is the intercept of the wt. fraction comonomer versus

$$\log\left(\frac{MW_w}{MW_n}\right)_{max.}$$

plot for a given comonomer type, where

$$\left(\frac{MW_w}{MW_n}\right)_{max.}$$

is the ratio of wt. ave. mol. wt. to no. ave. mol. wt. at the MWD boundary for a given comonomer type,
C_2 is the slope of the wt. fraction comonomer versus

$$\log\left(\frac{MW_w}{MW_n}\right)_{max.}$$

plot for a given comonomer type,

[0024] Since product performance is intimately related to molecular weight distribution (for example, narrow molecular weight distributions are generally required for excellent copolymer transparency, and a relatively broad MWD is usually required for excellent extrusion coating properties), the ability to prepare a wide range of distinct distributions at a single product melt index allows the manufacture of products suitable for a wide range of film, coating, molding and laminating applications.

[0025] Although the exact position of a MWD boundary depends upon comonomer concentration and a number of other variables, tests as above will demonstrate that the position is well above the corresponding phase boundary for the given comonomer concentration. For example, the MWD boundary occurs > 14 M Pa (>2000 psi) above, and >15° above, the phase boundary when producing an ethylene/acrylic acid copolymer containing nine percent acrylic acid by weight.

[0026] In addition to the ability to "tailor" the desired molecular weight distributions and achieve improved transparency and coating properties, in accordance with the present invention, "single-phase" products prepared just below, at, or above the MWD boundary possess less microgels or grain than comparable "two-phase" products as well as less grain than the non-random, "single-phase" products prepared e.g. in U.S. 4,248,990. In fact, at or above a corresponding MWD boundary, completely "grain free" products can be readily prepared. This reduction in microgels or "grain" has an aesthetic appeal, and the presence of excessive amounts of grain can contribute to inadequate heat seal and hot tack strengths, as well as promote delamination by compromising the adhesiveness. The improved heat seal and hot tack strengths of these "single-phase" products is also an object of this invention.

[0027] According to the present invention the copolymers can be conveniently prepared at reactor pressures from about 126.5 to about 351.5 M Pa (about 18,000 to about 50,000 psi) and at reactor temperatures from about 150° to about 350° C so long as the phase boundary conditions are appreciably exceeded. The preferred reactor is a continuous

autoclave with a 1:1 to about a 16:1 UD ratio. The reactor may consist of one or more reaction zone(s) by installing baffling systems common in the art; the reactor may be in series with one or more other reactors and the reactor may also be provided with one or more comonomer entry point(s) as described by British Patent 1,096,945. Hence, when more than one reaction zone is employed, the reactor-(s) can be maintained to provide an "intrazone" and/or "interzone" constant environment or it is also possible to operate in such a manner that a gradient of environments exists between and/or within the zones and/or reactors.

[0028] The products can be prepared with or without the use of solvents or hydrocarbons as telogens and/or carriers for the comonomer(s) and/or initiator(s). These products are also useful as base resins for the preparation of ionic copolymers, known in the art as "Ionomers", wherefrom additional improvements in transparency, chemical resistance and hot tack strength are readily obtained.

[0029] The gels that often characterize ethylene/carboxylic acid interpolymers can be of many different shapes, varying sizes and of more than one origin. For instance, microgels or "grain" (i.e., very small and fine gels) are shown in accordance with this disclosure to be an attribute of operating within and/or in the close proximity of a respective phase boundary; large gels (i.e., gels >25μ in diameter) are usually an attribute or the result of thermal oxidation/degradation; however, microgels or "grain" can actually "seed" these larger gels.

[0030] In this disclosure, the following gel rating is used:

EAA GEL RATING*	
Rating	Criteria
0	No visible gels
1	Very few microgels
2	Some microgels
3	Some microgels, some large gels
4	Numerous microgels, some large gels
5	Numerous microgels, numerous large gels
6	Severe gels
(* Rating according to criteria by visual inspection of blown film samples.)	

[0031] The following examples are to illustrate embodiments of the present invention, but the invention is not limited to the embodiments illustrated.

EXAMPLE 1 (for comparison purposes)

[0032] A 38um (1.5 mil) blown film was prepared from an ethylene/acrylic acid copolymer that contained 6.5 percent acrylic acid by weight and had a 2.5 g/10 min melt index (ASTM D1238E). The copolymer was prepared about 0-3.5 M Pa (about 0-500 psi) above and about 0-15 °C above its respective phase boundary and the film exhibited excessive microgels or "grain", a Gardner clarity of 12 percent transmission, a 20° film gloss of 25 percent reflected light, a film haze of 5.5 percent scattered light, a heat seal strength, at a 154°C (310°F) sealing bar temperature, of 0.57 kg/cm (3.2 lbs/in) width and a hot tack strength, at a 149°C (300°F) sealing bar temperature, of 59 g/cm (150 grams/inch).

EXAMPLE 2

[0033] Conversely, a 6.5 percent acrylic acid (by wt.) copolymer having the same melt index was prepared about 24.5 to about 31.5 M Pa (about 3500 to about 4500 psi) above and about 16 to about 18°C above its corresponding phase boundary. The resultant blown film of this product had a Gardner clarity of 47 percent, a 20° gloss of 45 percent, a film haze of 3.2 percent, negligible microgels or "grain", a 0.87 kg/cm (4.9 lbs/in) heat seal strength at 154°C (310 °F) and a 78.7 g/cm (200 g/in) in hot tack at 149 °C (300 °F). Both samples were fabricated into 38.1 μm (1.5 mil) film on an NRM 20/1, UD extruder that was equipped with an air ring, mandrel, annular die, and a take-off unit. Both fabrications maintained 204 °C melt temperature with a 2.25:1 blow-up ratio.

[0034] Data for the above examples and for additional samples of ethylene/acrylic acid copolymers are shown in the following tables. Whereas Examples 1, 5, 8, 11 and 15 are examples of prior art used in making non-random copolymers at 0-3.5 M Pa (0-500 psi) above, and 0-15°C above, the phase boundary, the remaining examples illustrate various embodiments of the present invention, all of which were produced at a temperature above the phase boundary temperature.

TABLE I

	EXAMPLE 1+	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4
Percent Acrylic Acid ±0.25	6.5[a]	6.5[a]	6.5[b]	6.5[b]
Melt Index g/10 min ±0.25	2.5	2.5	2.5	2.5
MWw/MWn (GPC)*	7.9	10.2	10.2	9.01
Synthesis Pressure Above Phase Boundary (psi) MPa	(0-500) 0-3.5	(3500-4500) 24.5-31.5	(3500-4500) 24.5-31.5	(7500-8500) 52.5-78.5
Blown Film Properties				
Gardner Clarity, % Transmission	10.9	47.1	72.1	69.4
20° Film Gloss, % Reflected	22.5	45.1	110.5	126.6
Percent Haze, % Scattered	5.42	3.2	1.59	1.03
Gel Rating Heat Seal Strength	4	0	0	0
@ (310°F, lb/in) 154°C, kg/cm	(3.0) 0.535	(4.9) 0.87	- -	- -
Hot Tack Strength @ (300°F,g/in) 149°C, g/cm	(150) 59	(200) 78.7	- -	- -

[a] Blown Film Fabrication: 204°C, 2.25 BUR, 38.1 μm (1.5 mil) thickness, NRM extruder

[b] Blown Film Fabrication: 218°C, 3.06 BUR, 38.1 μm (1.5 mil) thickness, NRM extruder

* GPC refers to gel permeation chromatography for determining molecular wt. distribution.

+ Comparative Example

TABLE II

	EXAMPLE 5 +	EXAMPLE 6	EXAMPLE 7
Percent Acrylic Acid ±0.3	9.0	9.0	9.0
Melt Index g/10 min ±0.25	3.0	3.0	3.0
MWw/MWn (GPC)	6.6	8.5	9.5
Synthesis Pressure Above Phase Boundary (psi) MPa	(0-500) 0-3.5	(2000-3000) 14-21	(3500-4500) 24.5-31.5
Blown Film Proverties a			
Gardner Clarity, % Transmission	13.3	24.1	48.1
20° Film Gloss, Reflected	32.4	41.6	70.5
45° Film Gloss, Reflected	65.1	62.2	81.9
Percent Haze, Scattered	4.2	3.5	1.91
Gel Rating	5	3	2
Heat Seal Strength @ (310°F, lb/in) 154°C, kg/cm	(3.2) 0.57	(5.4) 0.96	(>6.0)>1.07
Hot Tack Strength @ (300°F, g/in) 149°C, g/cm	(150) 59	(205) 80.7	(250) 98.4

[a] Blown Film Fabrication Conditions: 204°C, 2.25 BUR, 38.1 μm (1.5 mils) (thickness), NRM Extruder

+ Comparative Example

TABLE III

	EXAMPLE 8 +	EXAMPLE 9	EXAMPLE 10
Percent Acrylic Acid ±0.25	9.0	9.0	9.0
Melt Index g/10 min ±0.25	3.0	3.0	3.0
MW_w/MW_n (GPC)	6.5	9.5	8.9.
Synthesis Pressure Above MWD Boundary (psi) MPa	(4500-3500)* 31.5-24.5	(0-500) 0-3.5	(2800-3800) 19.6-26.6
Synthesis Pressure Above Phase Boundary (psi) MPa	(0-500) 0-3.5	(3500-4500) 24.5-31.5	(6800-7800) 47.6-59.6
Blown Film Properties [c]			
Gardner Clarity, %Transmission	12.1	26.1	36.5
20° Film Closs, % Reflected	14.6	13.3	23.0
45° Film Gloss, % Reflected	52.1	48.3	61.8
Repeat Haze	6.47	7.55	5.1
Gel Rating	5	3	1.5

[c] Gloucester Fabrication Conditions : 2-1/2" Extruder, 204°C melt temp., 2.75 BUR, 38.1 μm (1.5 mil) thick-film, 2 4/1 L/D

* Connotes 31.5-24.5MPa (4500-3500 psi) below MWD boundary.

+ Comparative Example

TABLE IV

	EXAMPLE 11+	EXAMPLE 12	EXAMPLE 13	EXAMPLE 14
Percent Acrylic Acid ±0.25	6.5	6.5	6.5	6.5
Melt Index g/10 min ±0.25	5.5	5.5	5.5	5.5
MWw/MWa (GPC)	7.1	10.1	13.7	10.2
Synthesis Pressure Above MPa Phase Boundary (psi) MPa	0-3,5 (0-500)	24,5-31,5 (3500-4500)	38,5-45,5 (5500-6500)	52,5-51,5 (7500-8500)
Synthesis Pressure Above MWD Boundary (psi) MPa	45,5-38,5* (6500-5500)*	17,5-10,5* (2500-1500)*	±3,5 ±500	10,5-17,5 (1500-2500)
Extrusion Coating Properties [d]				
Neck-in @ (440 fpm) (inches) 134m/min cm	- -	4,45 (1.75)	4,14 (1.63)	4,75 (1.37)
Nip Speed (fpm) m/min	61 (200)	158,5 (520)	161,5 (530)	302 (992)
Draw-down Speed (fpm) m/min	222,5 (730)	327,7 (1015)	381 (1250)	>457 (>1500)
Minimum Coating (mils) μm	55,9 (2.2)	21,6 (0.85)	21,1 (0.83)	11,2 (0.44)
Gel Rating	5	2	1	0
Hell Seal Strength, @ (310°F,)(lb/in) width 154°C,kg/cm	0,41 (2.3)	0,39 (2.2)	>0,7 (>3.9)	>0,71 (>4.0)
Hot Tack Strengh, @ (300°F,) (g/in) width 149°C, g/cm	98,4 (250)	133,8 (340)	275,6 (700)	295,3 (750)

Table continued

Extrusion Coating Properties [d]				
A1 Adhesion, kg/cm (1b/in) width	0.143 (0.80)	1,134 (0.75)	0,212 (1.22)	- -

[d] Black Clawson Extrusion Coater (3-1/2" extruder, 30/1 L/D); melt temperature 288°C (550°F) screw speed 85 RPM, air gap (6 inches) 15.24 cm

* cannotes MPa (psi) below the MWD boundary

+ Comparative Example

TABLE V

	EXAMPLE 15 +	EXAMPLE 16
Percent Acrylic Acid ±0.3	9.0	9.0
Melt Index g/10 min ±0.25	12.0	12.0
MWw/MWn (GPC)	6.5	9.2
Synthesis Pressure Above Phase Boundary (psi) MPa	0-3,5 (0-500)	24,5-31.5 (3500-4500)
Synthesis Pressure below MWD Boundary (psi) MPa	31,5-24,5* (4500-3500)*	±3,5 (±500)
Extrusion Coating Properties[d]		
Nip Speed (fpm) m/mm	(266) (875)	388,6 (1275)
Draw-down Speed (fpm) m/mm	396,2 (1300)	> 451 (>1500)
Minimum Coating (mils) μm	12,7 (0.50)	8,89 (0.35)
Sealing Properties .		
Heat Seal Strength @ (260°F) 127°C,(lb/in) kg/cm	0,80 (4.5)	>0,73 (>4. 1)
Hot Tack Strength @ (300°F) 149°C,(g/in) g/cm	137,8 (350)	334,6 (850)

[d] Black Clawson Extrusion Coater. (3-1/2" extruder, 30/1 L/D); melt temperature 288°C (550°F) screw speed 85 RPM air gap (6 inches) 15,24 cm

* connotes MPa (psi) below MWD boundary

+ Comparative Example

Claims

1. A process for producing homogeneous, random inter-polymers of ethylene and at least one olefinically unsaturated comonomer selected from the group comprising acrylates,methacrylates, vinyl esters and olefinically unsaturated carboxylic acids,
said process comprising inter-polymerizing the monomers in a substantially constant environment, under steady state conditions, in a single-phase reaction mixture, under the influence of a free-radical initiator, and in a well-stirred autoclave reactor operated in a continuous manner as the monomers are fed into the reactor and the reaction mixture is withdrawn, said process being **characterized by**
the use of synthesis conditions of temperature and pressure which are elevated to a level high enough above the phase boundary between two-phase and single-phase operation such that the molecular weight distribution (MWD) boundary is reached, or surpassed, the said molecular weight distribution boundary being the highest ratio of weight average molecular weight/number average molecular weight obtainable in single-phase operation, said elevated pressure being greater than 14 M Pa (2000 psi) above, and said elevated temperature being greater than 15° C above the synthesis conditions required at the phase boundary for a given mixture of ethylene and comonomer, thereby producing an interpolymer having less gels and/or grain.

2. The process of Claim 1 wherein the olefinically-unsaturated organic monomers comprise at least one of acrylic acid, methacrylic acid, alkyl acrylates, alkyl methacrylates, and vinyl esters.

3. The process of Claim 1 wherein the olefinically-unsaturated organic monomer comprises acrylic acid or methacrylic acid.

4. The process of Claim 1 wherein the olefinically-unsaturated organic monomer is acrylic acid.

5. The process of Claim 1 wherein the olefinically-unsaturated organic monomer is methacrylic acid.

6. The process of Claim 1 wherein the so-produced interpolymers comprise from about 99% to about 65% by weight of ethylene units in the polymer chain.

7. The process of claim 1 wherein the so-produced interpolymers comprise from about 99% to about 88% by weight of ethylene units in the polymer chain.

8. The process of Claim 1 wherein the synthesis conditions comprise an elevated temperature which is in the range of about 150°C to about 350° C and an elevated pressure which is in the range of about 126.5 to about 351.8 M Pa (about 18,000 to about 50,000 psi),
wherein said pressure is at least about 14 M Pa (2000 psi) above, and said temperature is above, the minimum amount needed to produce a single-phase reaction mixture and wherein elevated temperature and elevated pressure are sufficient to substantially exceed the temperature and pressure at which the molecular weight distribution boundary of the so-produced interpolymer is reached.

Patentansprüche

1. Verfahren zur Herstellung von homogenen, statistischen Interpolymeren von Ethylen und mindestens einem olefinisch ungesättigten Comonomer, ausgewählt aus der Gruppe, umfassend Acrylate, Methacrylate, Vinylester und olefinisch ungesättigte Carbonsäuren,
wobei das Verfahren das Interpolymerisieren der Monomere in einer im wesentlichen konstanten Umgebung, unter stationären Bedingungen, in einem einphasigen Reaktionsgemisch, unter dem Einfluß eines radikalischen Initiators und in einem ausreichend gerührten Autoklavreaktor, der auf kontinuierliche Weise so betrieben wird, daß die Monomere in den Reaktor zugeführt und das Reaktionsgemisch abgezogen wird, umfaßt, wobei das Verfahren **gekennzeichnet ist durch**
die Verwendung von Synthesebedingungen von Temperatur und Druck, die auf ein genügend hohes Niveau oberhalb der Phasengrenze zwischen einphasigem und zweiphasigem Betrieb angehoben sind, so daß die Grenze der Molekulargewichtsverteilung (MWD) erreicht oder überschritten wird, wobei die Grenze der Molekulargewichtsverteilung das höchste, bei einphasigem Betrieb erreichbare Verhältnis von Gewicht des mittleren Molekulargewichts zu Anzahl des mittleren Molekulargewichts ist, wobei der erhöhte Druck mehr als 14 MPa (2000 psi) über und die erhöhte Temperatur mehr als 15°C über den Synthesebedingungen ist, die an der Phasengrenze für ein gegebenes Gemisch aus Ethylen und Comonomer erforderlich sind, wodurch ein Interpolymer mit weniger Gelen und/oder Korn erzeugt wird.

2. Verfahren nach Anspruch 1, worin die olefinisch ungesättigten organischen Monomore mindestens eines von Acrylsäure, Methacrylsäure, Alkylacrylaten, Alkylmethacrylaten und Vinylestern umfassen.

3. Verfahren nach Anspruch 1, worin das olefinisch ungesättigte organische Monomer Acrylsäure oder Methacrylsäure umfaßt.

4. Verfahren nach Anspruch 1, worin das olefinisch ungesättigte organische Monomer Acrylsäure ist.

5. Verfahren nach Anspruch 1, worin das olefinisch ungesättigte organische Monomer Methacrylsäure ist.

6. Verfahren nach Anspruch 1, worin die so erzeugten Interpolymere von etwa 99 bis etwa 65 Gew.-% Ethyleneinheiten in der Polymerkette enthalten.

7. Verfahren nach Anspruch 1, worin die so erzeugten Interpolymere von etwa 99 bis etwa 88 Gew.-% Ethyleneinheiten in der Polymerkette enthalten.

8. Verfahren nach Anspruch 1, worin die Synthesebedingungen eine erhöhte Temperatur, die im Bereich von etwa 150°C bis 350°C ist, und einen erhöhten Druck umfassen, der im Bereich von etwa 126,5 bis etwa 351,8 MPa (etwa 18.000 bis etwa 50.000 psi) ist,
worin der Druck mindestens etwa 14 MPa (2000 psi) über und die Temperatur über der minimalen Höhe ist, die zur

Erzeugung eines einphasigen Reaktionsgemisches erforderlich ist, und worin erhöhte Temperatur und erhöhter Druck ausreichend sind, um die Temperatur und den Druck erheblich zu übersteigen, wo die Grenze der Molekulargewichtsverteilung des so erzeugten Interpolymers erreicht wird.

Revendications

1. Procédé de préparation d'interpolymères statistiques, homogè-nes, d'éthylène et d'au moins un comonomère à insaturation oléfinique, choisi dans l'ensemble comprenant les acrylates, les méthacrylates, les esters vinyliques et les acides carboxyliques à insaturation oléfinique,
ledit procédé comprenant l'interpolymérisation des monomères dans un environnement pratiquement constant, dans des conditions d'état stationnaire, dans un mélange réactionnel à une seule phase, sous l'influence d'un amorceur radicalaire, dans un réacteur autoclave bien agité que l'on fait fonctionner en continu tandis que les monomères sont introduits dans le réacteur et que le mélange réactionnel est extrait du réacteur,
ledit procédé étant **caractérisé par le fait que** l'on opère dans des conditions de synthèse (température et pression) qui sont amenées à un niveau suffisamment élevé au-dessus de la frontière entre les domaines correspondant à l'opération à deux phases et à l'opération à une seule phase (frontière de phase) pour que la limite de distribution des masses molaires (MWD) soit atteinte ou dépassée, ladite limite de distribution des masses molaires étant la valeur la plus élevée du rapport de la masse molaire moyenne en poids à la masse molaire moyenne en nombre que l'on peut obtenir dans une opération à une seule phase, ladite pression élevée étant supérieure de plus de 14 MPa (2000 psi) et ladite température élevée étant supérieure de plus de 15 °C aux conditions de synthèse requises à la frontière de phase pour un mélange donné d'éthylène et de comonomère, ce qui fournit un interpolymère ayant moins de gel et/ou de grain.

2. Procédé selon la revendication 1, dans lequel les monomères organiques à insaturation oléfinique comprennent au moins un composé pris parmi l'acide acrylique, l'acide méthacrylique, les acrylates d'alkyle, les méthacrylates d'alkyle et les esters vinyliques.

3. Procédé selon la revendication 1, dans lequel le monomère organique à insaturation oléfinique comprend l'acide acrylique ou l'acide méthacrylique.

4. Procédé selon la revendication 1, dans lequel le monomère organique à insaturation oléfinique est l'acide acrylique.

5. Procédé selon la revendication 1, dans lequel le monomère organique à insaturation oléfinique est l'acide méthacrylique.

6. Procédé selon la revendication 1, dans lequel les interpolymères ainsi produits comprennent d'environ 99 % à environ 65 % en poids de motifs éthylène dans la chaîne de polymère.

7. Procédé selon la revendication 1, dans lequel les interpolymères ainsi produits comprennent d'environ 99 % à environ 88 % en poids de motifs éthylène dans la chaîne de polymère.

8. Procédé selon la revendication 1, dans lequel les conditions de synthèse comprennent une température élevée, qui est située dans l'intervalle allant à peu près de 150 à 350 °C, et une pression élevée, qui est comprise dans l'intervalle allant à peu près de 126,5 à 351,8 MPa (environ 18 000 à 50 000 psi), ladite pression étant supérieure d'au moins environ 14 MPa (2000 psi) et ladite température étant supérieure aux valeurs minimales nécessaires pour la production d'un mélange réactionnel à une seule phase, et ladite température élevée et ladite pression élevée étant suffisantes pour dépasser sensiblement la température et la pression auxquelles la limite de distribution de masses molaires de l'interpolymère ainsi produit est atteinte.

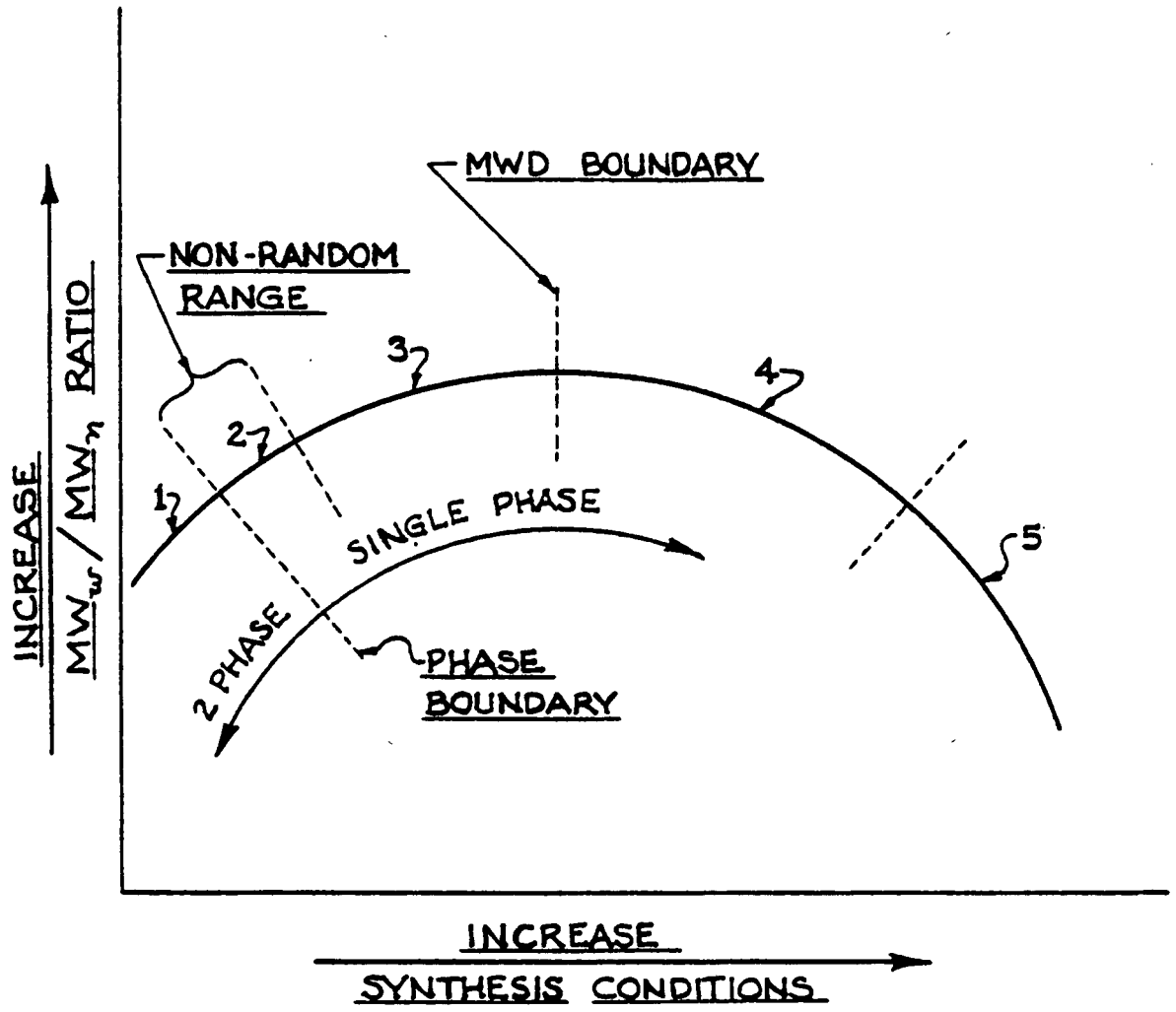
MWD BOUNDARY
NON-RANDOM RANGE
3
4
2
1
SINGLE PHASE
5
2 PHASE
PHASE BOUNDARY
INCREASE
MW_w / MW_n RATIO
INCREASE
SYNTHESIS CONDITIONS

Fig. 1